STRUCTURAL CHEMISTRY

ISSN: 2053-2296
journals.iucr.org/c

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Acta Cryst. (2018). C**74**, 564–570

Acta Cryst C STRUCTURAL CHEMISTRY

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Three new dihydro-β-agarofuran sesquiterpenes from the seeds of *Maytenus boaria*

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Received 20 February 2018
Accepted 6 April 2018

Edited by V. Langer, Chalmers University of Technology, Sweden

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Keywords: Celastraceae; Maytenus boaria; sesquiterpene; dihydro-β-agarofuran; crystal structure; NMR; DSC.

CCDC references: 1835260; 1835259; 1835258

Supporting information: this article has supporting information at journals.iucr.org/c

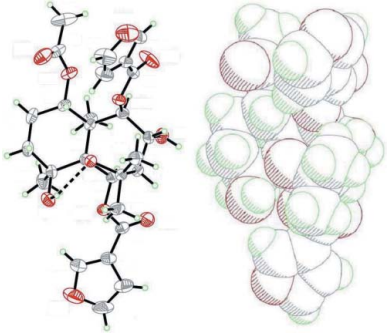
As part of a project studying the secondary metabolites extracted from the Chilean flora, we report herein three new β-agarofuran sesquiterpenes, namely (1*S*,4*S*,5*S*,6*R*,7*R*,8*R*,9*R*,10*S*)-6-acetoxy-4,9-dihydroxy-2,2,5a,9-tetramethyloctahydro-2*H*-3,9a-methanobenzo[*b*]oxepine-5,10-diyl bis(furan-3-carboxylate), $C_{27}H_{32}O_{11}$, (**II**), (1*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-6-acetoxy-9-hydroxy-2,2,5a,9-tetramethyloctahydro-2*H*-3,9a-methanobenzo[*b*]oxepine-5,10-diyl bis(furan-3-carboxylate), $C_{27}H_{32}O_{10}$, (**III**), and (1*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-6-acetoxy-10-(benzoyloxy)-9-hydroxy-2,2,5a,9-tetramethyloctahydro-2*H*-3,9a-methanobenzo[*b*]-oxepin-5-yl furan-3-carboxylate, $C_{29}H_{34}O_9$, (**IV**), obtained from the seeds of *Maytenus boaria* and closely associated with a recently published relative [Paz *et al.* (2017). *Acta Cryst.* C**73**, 451–457]. In the (isomorphic) structures of (**II**) and (**III**), the central decalin system is esterified with an acetate group at site 1 and furoate groups at sites 6 and 9, and differ at site 8, with an OH group in (**II**) and no substituent in (**III**). This position is also unsubstituted in (**IV**), with site 6 being occupied by a benzoate group. The chirality of the skeletons is described as 1*S*,4*S*,5*S*,6*R*,7*R*,8*R*,9*R*,10*S* in (**II**) and 1*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S* in (**III**) and (**IV**), matching the chirality suggested by NMR studies. This difference in the chirality sequence among the title structures (in spite of the fact that the three skeletons are absolutely isostructural) is due to the differences in the environment of site 8, *i.e.* OH in (**II**) and H in (**III**) and (**IV**). This diversity in substitution, in turn, is responsible for the differences in the hydrogen-bonding schemes, which is discussed.

1. Introduction

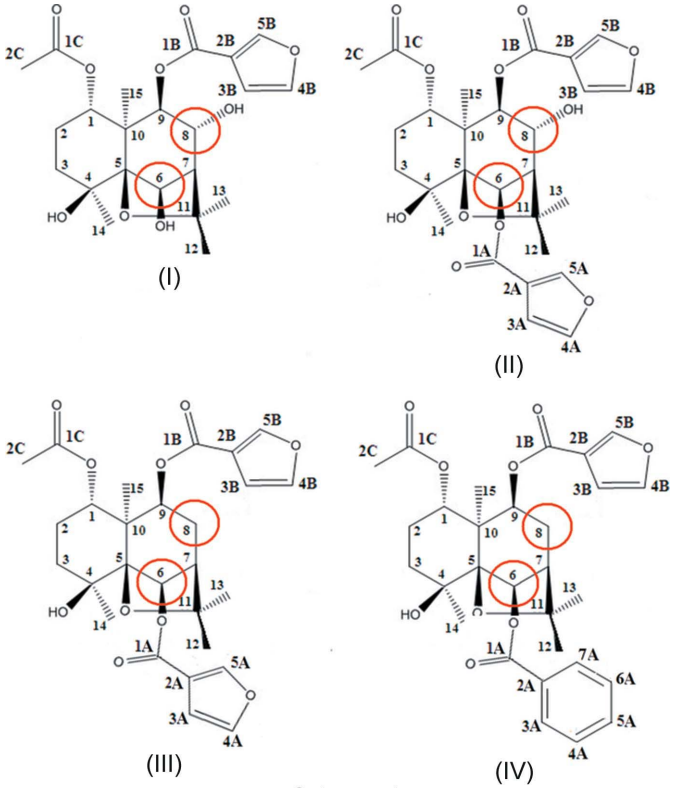
Celastraceae is a populous family constituted by more than 90 genera and 1400 species, embracing a broad list which includes a variety of tropical and subtropical trees, shrubs and vines. From an extractive point of view, the family is highly significant, in particular as a source of sesquiterpenes with a dihydro-β-agarofuran skeleton, which is perhaps the most characteristic and widespread group of secondary metabolites present in the Celastraceae family.

For years this group of sesquiterpenes has attracted the interest of organic chemists due to the broad range of medical and biological properties (see, for instance, Mbaning *et al.*, 2013; Céspedes *et al.*, 2001; Calderón *et al.*, 2001, among many others).

The particular attention given to these sesquiterpenes has resulted in a large number of reports, even if only a reduced subgroup included a crystal structure analysis, in spite of the fact that the latter plays an almost irreplaceable role for



looking for structure–property correlations, or trying to find common structural patterns in related compounds from a similar origin. Even if much information can be obtained from spectroscopic methods (mostly NMR), the X-ray structural determination, when feasible, provides the definite answer.



Scheme 1

As part of recent structural work, we have made a literature survey of sesquiterpenes with a reported crystal structure, to which we refer the interested reader (Paz *et al.*, 2017).

The Celastraceae family is broadly diseminated over the world and is found in South America (mainly Argentina and Chile) in the endemic genus *Maytenus*, occurring in four different species, *i.e. M. magellanica*, *M. disticha*, *M. chubutensis* and *M. boaria*. The last named, also called 'maiten', is an evergreen tree with lanceolate leaves about 1 to 3 cm wide and 3 to 9 long, and is characterized by a grey bark trunk which can reach up to 25 m in height and 1 m in diameter. The seeds of *Maytenus boaria* are known to be rich in natural products, and many reports on the subject disclosed a number of highly oxygenated sesquiterpenes with a dihydroagarofuran skeleton, as determined by one- and two-dimensional NMR (*e.g.* Alarcón *et al.*, 1995). It is to be noted that the curative properties of the plant were already well known and thoroughly used by the ancient inhabitants of the Araucania.

As part of a long-range project on natural products from the Chilean flora, and with the idea that there were further Agarofuran species obtainable from *M. boaria* which have not yet been unveiled, we engaged in new extractive attempts using this plant. A preliminary successful result of this study was the recently reported structure of a new sesquiterpene, *i.e.* (1*S*,4*S*,5*S*,6*R*,7*R*,8*R*,9*R*,10*S*)-6-acetoxy-4,9,10-trihydroxy-2,2,5a,9-tetramethyloctahydro-2*H*-3,9a-methanobenzo[*b*]oxepin-5-yl furan-3-carboxylate [hereinafter (**I**)] (Paz *et al.*, 2017).

Confirming *M. boaria* as an almost unexhaustable source of new intriguing agarofurans, we have now been able to isolate from the same extracts three new dihydroagarofuranes, closely related to (**I**), which crystal and molecular structures we report herein, *viz.* (1*S*,4*S*,5*S*,6*R*,7*R*,8*R*,9*R*,10*S*)-6-acetoxy-4,9-dihydroxy-2,2,5a,9-tetramethyloctahydro-2*H*-3,9a-methanobenzo[*b*]oxepine-5,10-diyl bis(furan-3-carboxylate), (**II**), (1*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-6-acetoxy-9-hydroxy-2,2,5a,9-tetramethyloctahydro-2*H*-3,9a-methanobenzo[*b*]oxepine-5,10-diyl bis(furan-3-carboxylate), (**III**), and (1*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-6-acetoxy-10-(benzoyloxy)-9-hydroxy-2,2,5a,9-tetramethyloctahydro-2*H*-3,9a-methanobenzo[*b*]oxepin-5-yl furan-3-carboxylate, (**IV**).

2. Experimental

2.1. Extraction, purification and crystallization

Dihydro-β-agarofuran sesquiterpenoids (**II**), (**III**) and (**IV**) (see Scheme 1) were isolated from an ethyl acetate extract of the crushed seeds of the tree *Maytenus boaria*. The seeds were collected in Temuco, IX Region of Chile, in September 2016.

The seeds (1.3 kg) were crushed and extracted by maceration with ethyl acetate (EtOAc) for 3 d. The organic solvent was evaporated *in vacuo*, giving a crude extract (600 g, orange oil), which was further fractionated by silica-gel column chromatography (CC), giving a primary fractioning of nine fractions (F1–F9) using increasing polarity from hexane to ethyl acetate. Fractions F1 to F4 displayed carotenoids, unsaturated fatty acids and β-sitosterol, but no sesquiterpenes were detected. A subsequent purification of F7 by CC with hexane–ethyl acetate (2:1 *v*/*v*) gave two solids which were recrystallized from EtOAc, giving 55 mg of (**III**) (0.0092% yield) and 32 mg of (**IV**) (0.0053% yield). Fraction F8, after CC (with hexane–ethyl acetate 1:1 *v*/*v*), was purified by Sephadex LH-20 giving 150 mg of (**II**) (0.025% yield). All three compounds were recrystallized by slow evaporation at 293 K from a 1:1 (*v*/*v*) methanol–ethyl acetate solution as colourless crystals suitable for single-crystal X-ray diffraction.

2.2. Refinement

All H atoms were identified in an intermediate difference map and treated differently in the refinement. H atoms on C atoms were idealized and allowed to ride both with respect to their coordinates and their displacement parameters, the latter taken as $U_{iso}(H) = xU_{eq}(C)$, with C—H = 0.93 Å and x = 1.2 for aromatic, C—H = 0.97 Å and x = 1.2 for methylene, and C—H = 0.96 Å and x = 1.5 for methyl groups. H atoms attached to O atoms were refined with restrained O—H distances of 0.85 (1) Å and x = 1.2. In (**IV**), the furan O atom presents a displacement ellipsoid slightly larger than that of its neighbour, probably due to some rotational disorder of the whole group. No modelling for this effect was attempted. In addition, structure (**IV**) presents small voids, about 60 Å^3 in volume. Even if, in principle, this is compatible with a small

Table 1
Experimental data.

Crystal system: monoclinic; space group: $P2_1$; T (K): 294; Z: 2; λ (Å): 0.7107 (Mo $K\alpha$); diffractometer: Oxford Diffraction Xcalibur CCD Eos Gemini; absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009); '$(\sin\theta/\lambda)_{max}$ (Å^{-1})': 0.625; H atoms treated by a mixture of independent and constrained refinement; absolute structure assigned by comparison with related compounds of the same origin.

	(**II**)	(**III**)	(**IV**)
Crystal data			
Chemical formula	$C_{27}H_{32}O_{11}$	$C_{27}H_{32}O_{10}$	$C_{29}H_{34}O_9$
M_r	532.52	516.52	526.56
Temperature (K)	294	294	294
a, b, c (Å)	11.2664 (3), 9.6575 (3), 12.0758 (4)	11.2999 (3), 9.6363 (3), 12.1306 (4)	7.9045 (4), 9.2038 (5), 19.3935 (9)
β (°)	98.262 (3)	97.539 (3)	93.073 (4)
V (Å^3)	1300.28 (6)	1309.47 (7)	1408.88 (12)
Density (Mg m^{-3})	1.360	1.310	1.241
Data collection			
μ (mm^{-1})	0.11	0.10	0.09
Crystal size (mm)	0.28 × 0.18 × 0.14	0.42 × 0.22 × 0.12	0.50 × 0.23 × 0.20
T_{min}, T_{max}	0.95, 0.98	0.95, 0.98	0.96, 0.99
Refinement			
N_{meas}, N_{indep}, $N_{[I > 2\sigma(I)]}$	31774, 5295, 4103	31770, 5337, 4297	24363, 5718, 3559
R_{int}	0.053	0.047	0.099
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.117, 0.95	0.039, 0.093, 1.04	0.060, 0.152, 1.00
No. of reflections	5295	5337	5718
No. of parameters	356	343	352
No. of restraints	3	2	2
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.13, −0.19	0.12, −0.16	0.16, −0.15
Thermal behaviour			
T_f(onset) (K)	526	481	499
ΔH_f (kJ mol^{-1})	44 (1)	34 (2)	17 (2)
Optical rotation			
$[\alpha]_D$	− 6.6	−5.4	−3.2
Concentration (c), solvent	0.5, $CHCl_3$	0.4, MeOH	0.2, MeOH

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

disordered solvent molecule (*e.g.* methanol), the electron density within the hole would not support this hypothesis.

The use of Mo $K\alpha$ radiation rendered the discrimination of the absolute structure impossible (the heaviest atom is O), for which the assignment was made by matching it with the reported configuration of all the related structures analyzed in Paz *et al.* (2017).

2.3. Physicochemical measurements

^{1}H NMR spectra were measured on a Bruker Avance III spectrometer (Bruker Biospin GmbH, Rheinstetten, Germany), using CD_2Cl_2 as solvent and its residual peaks as internal references (5.32 ppm for ^{1}H). Differential scanning calorimetry (DSC) was performed with a Shimadzu DSC-50 apparatus, all the experiments being carried out on individual single crystals using aluminium pans, at a heating rate of 5 K min^{-1}. Optical rotations were measured at 298 K in a 1 dm cell with a PerkinElmer 343 polarimeter.

3. Results

3.1. NMR spectroscopy

The molecular structures of all three title compounds were determined by this technique (data summarized in Table ST1 of the supporting information) and they agree with the subsequent X-ray results. All the structures show five singlet methyl signals, four of them from the sesquiterpenoid core and one from the acetyl group at 1.72 ppm, that correlate with the carbonyl group at 170.2 ppm. Other carbonyl groups are displayed at C-9 [162 ppm for (**III**) and (**IV**)] and C-6, *i.e.* at 162.4 ppm (furoyl) for (**III**) and at 166.1 ppm (benzoyl) for (**IV**).

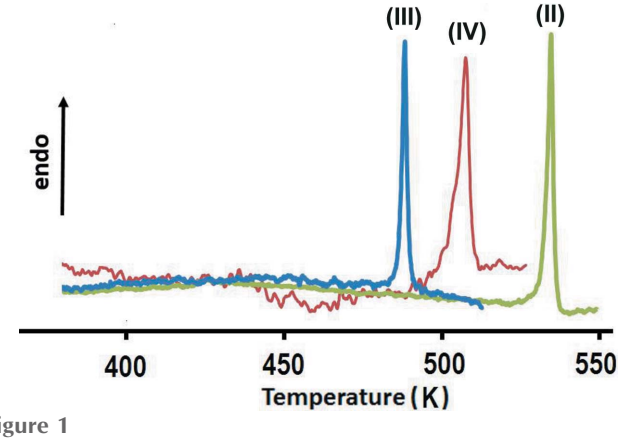


Figure 1
DSC diagrams for (**II**)–(**IV**).

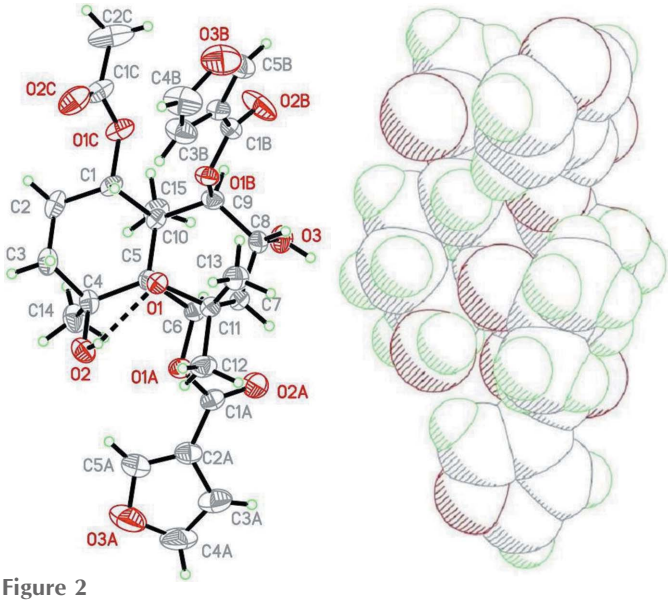


Figure 2
Two molecular representations of (**II**), showing (*a*) a displacement ellipsoid plot, with ellipsoids drawn at the 40% probability level, and (*b*) a space-filling view.

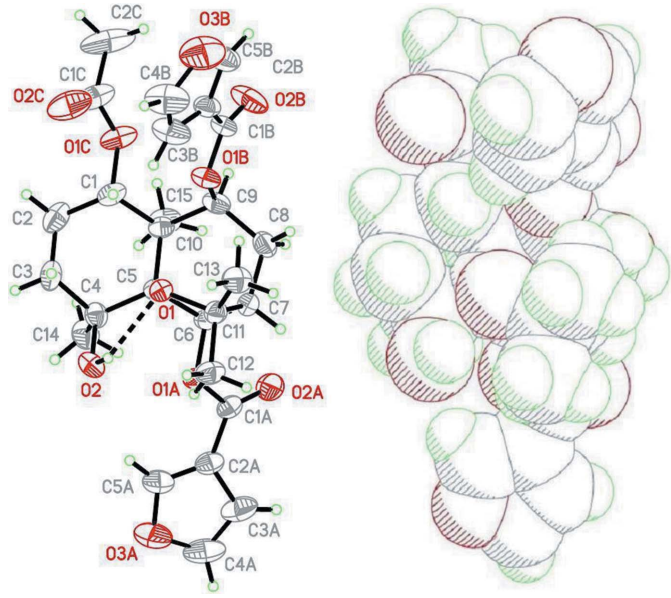


Figure 3
Two molecular representations of (**III**), showing (*a*) a displacement ellipsoid plot, with ellipsoids drawn at the 40% probability level, and (*b*) a space-filling view.

The relative stereochemistry has been established from a study of the coupling constants in the ^{1}H NMR spectrum. Mbaning *et al.* (2016) reported a J = 7.3 Hz for the axial H9 atom. Compound (**III**) has a J = 6.6 Hz for atom H9, while compound (**IV**) has a J = 6.7 Hz for the same correlation, confirming the stereochemistry of C9 (*R*). This was later confirmed by the X-ray structure determination.

3.2. DSC and optical rotation

Thermal data from differential scanning calorimetry (DSC; Fig. 1) show for (**IV**) an endothermic peak on heating (T_{onset} = 499 K and ΔH = 17 kJ mol^{-1}) and its overcooled exothermic counterpart (T_{onset} = 404 K and ΔH = 14 kJ mol^{-1}). On the other hand, for each of (**III**) and (**II**), only one detectable event on heating ascribed to melting and decomposition was observed [T_{onset} = 481 K and ΔH = 34 kJ mol^{-1} for (**III**); T_{onset} = 526 K and ΔH = 44 kJ mol^{-1} for (**II**)].

Optical rotation measurements were performed in different solvents, and resulted in a $[\alpha]_D$ value of −6.6 (*c* 0.5, $CHCl_3$) for (**II**), −5.4 (*c* 0.4, MeOH) for (**III**) and −3.2 (*c* 0.2, MeOH) for (**IV**), where $[\alpha]_D$ is the specific rotation, corresponding to the sodium *D* line, and *c* is the (adimensional) concentration, normalized so that n = 1 corresponds to a (real) concentration of 10 mg ml^{-1} (for further details, see the 'Gold Book'; IUPAC, 1997).

The rather low n values are due to extremely low sample availability.

3.3. Crystal structure

Table 1 presents the crystal, refinement and some further experimental data for the three title structures, while Figs. 2–4 show their molecular representations, the leftmost diagrams in the form of an ellipsoid plot and the rightmost as a space-filling view.

Table 2 presents the most significant hydrogen-bonding interactions in the structures. In this table, the first column corresponds to an identification code, while the two rightmost columns correspond to the results of AIM (atoms in molecules) analysis (Bader, 1990) presented in the form of the electron density [$\rho(r)$] and its Laplacian [$\nabla^2\rho(r)$], calculated at the bond critical points (BCP) and which serve for an evaluation of their comparative relevance. Further information on the AIM theory is given as supporting information.

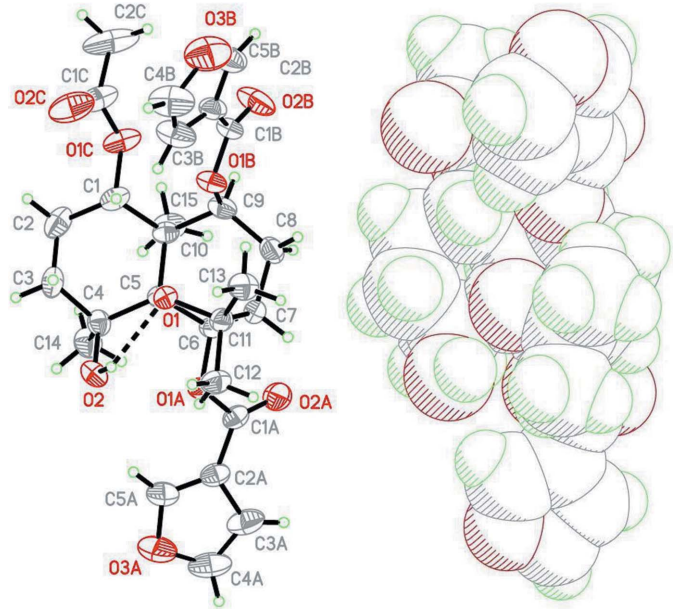


Figure 4
Two molecular representations of (**IV**), showing (*a*) a displacement ellipsoid plot, with ellipsoids drawn at the 40% probability level, and (*b*) a space-filling view.

Table 2
Hydrogen-bonding interactions (Å, °).

AIM analysis of the electron density was performed at the PBEPBE-D/DGDZVP level of theory using the *Multiwfn* program (Lu & Chen, 2012).

	Code	D—H···A	D—H	H···A	D···A	D—H···A	$100\rho(r)$ (a.u.)	$100\nabla^2\rho(r)$ (a.u.)
(II)	#1	O2—H2···O1	0.85 (3)	2.10 (3)	2.623 (3)	119 (3)	2.23	1.01
	#2	C12—H12*C*···O1*A*	0.96	2.23	2.943 (4)	130	1.64	0.63
	#3	C13—H13*A*···O1*B*	0.96	2.21	3.029 (4)	142	1.65	0.62
	#4	C14—H14*A*···O1*A*	0.96	2.39	3.023 (4)	123	1.24	0.47
	#5	O3—H3···O2*C*^{i}	0.85 (3)	2.17 (2)	2.945 (4)	152 (4)	1.39	0.58
	#6	C5*B*—H5*B*···O2^{ii}	0.93	2.37	3.284 (5)	168	1.04	0.37
(III)	#1	O2—H2···O1	0.86 (3)	2.08 (3)	2.625 (2)	121 (2)	2.4	1.02
	#2	C12—H12*C*···O1*A*	0.96	2.25	2.949 (3)	129	1.6	0.62
	#3	C13—H13*A*···O1*B*	0.96	2.23	3.048 (3)	142	1.58	0.59
	#4	C14—H14*A*···O1*A*	0.96	2.41	3.046 (4)	123	1.21	0.45
	#5	C4*A*—H4*A*···O2*C*^{i}	0.93	2.56	3.376 (5)	146	0.75	0.25
	#6	C5*B*—H5*B*···O2^{ii}	0.93	2.40	3.310 (4)	167	0.97	0.34
(IV)	#1	O2—H2···O1	0.84 (2)	2.26 (4)	2.641 (4)	108 (4)	2.15	0.98
	#2	C12—H12*C*···O1*A*	0.96	2.16	2.898 (7)	132	1.67	0.65
	#3	C13—H13*A*···O1*B*	0.96	2.24	3.070 (7)	144	1.57	0.59
	#4	C14—H14*A*···O1*A*	0.96	2.45	3.085 (7)	124	1.19	0.43
	#5	O2—H2···O2*B*^{i}	0.84 (2)	2.33 (3)	3.118 (5)	155 (4)	1.02	0.39
	#6	C9—H9···O2^{ii}	0.98	2.45	3.335 (5)	150	0.94	0.33

Note: (*) Paz *et al.* (2017). Symmetry codes for (**II**): (i) $x, y+1, z$; (ii) $x-1, y, z$. Symmetry codes for (**III**): (i) $x+1, y+1, z$; (ii) $x-1, y, z$. Symmetry codes for (**IV**): (i) $x+1, y, z$; (ii) $x-1, y, z$.

Table 3
Chiral centres in (**I**), (**II**), (**III**) and (**IV**).

	(**I**)*	(**II**)	(**III**)	(**IV**)
C1	*S*	*S*	*S*	*S*
C4	*S*	*S*	*S*	*S*
C5	*S*	*S*	*S*	*S*
C6	*R*	*R*	*R*	*R*
C7	*R*	*R*	*R*	*R*
C8	*R*	*R*	n.a.	n.a.
C9	*R*	*R*	*S*	*S*
C10	*S*	*S*	*S*	*S*

Note: (*) Paz *et al.* (2017).

The molecules are built up around a typical dihydro-β-agarofuran skeleton, esterified with an acetate group at site 1 and a furoate group at site 9, as is their close relative (**I**) (see Scheme 1 for the numbering of the skeleton). Differences arise at sites 6 and 8, with OH/OH groups in (**I**), fuorate/OH groups in (**II**), fuorate/H groups in (**III**) and benzoate/H groups in (**IV**). In particular, the decalin skeleton in all four compounds, and the particular disposition of the sustituents which they have in common, are absolutely congruent and match each other to a few tenths of an Ångstrom. The chirality sequence for (**I**)–(**IV**) is presented in Table 3.[1]

As in (**I**), the central decalin moiety (atoms C1–C10) appears in its *trans* form (H5 at C5 and H10 at C10 being antiparallel to each other), with both cyclohexane groups in chair conformations and methyl atoms C14 and C15 on the same side of the plane. In what follows, values separated by '/' will denote a (**II**)/(**III**)/(**IV**) sequence.

Thus, the mean planes through the equatorial sites in each chair [that through atoms C5, C10, C2 and C3, with mean deviations of 0.030 (2)/0.033 (3)/0.030 (5) Å, and that through atoms C5, C10, C7 and C8, with mean deviations of 0.016 (2)/0.020 (4)/0.015 (4) Å] form dihedral angles of 164.5 (3)/163.5 (3)/164.1 (5)°, respectively, confirming their nearly planar disposition.

4. Discussion

As shown above, the inner skeleton in (**II**), (**III**) and (**IV**) is identical to that in (**I**) and, as already shown in Paz *et al.* (2017), to the 19 remaining molecular skeletons in the literature therein compared, is indicative of the robustness of the group, irrespective of the substituents present.

It is interesting to compare the packing motifs resulting from hydrogen bonding with that in close relative (**I**). The structural differences leading to hydrogen-bonding diversity rely on the existence of a different number of efficient OH donors attached to the decalin skeleton, *viz.* in structure (**I**), there are three of these groups, namely O2 at C4, O1*A* at C6 and O3 at C8 (see Scheme 1). Compound (**II**) has only two (O2 and O3) and compounds (**III**) and (**IV**) have only one (O2).

[1] A (perhaps rather naive) point of view could suggest that this absolutely identical backbone configuration should lead, in principle, to an also identical set of chirality descriptors. However, when comparing the results provided by *PLATON* (Spek, 2009), the (in principle puzzling) results presented in Table 3 are obtained, *viz.* sites 1–7 and 10 agree, as expected. On the other hand, the difference at site 8 is also to be expected, since no chirality can be ascribed for (**III**) and (**IV**), as the site is not subtituted. The puzzling point is C9, which occupies a position where all four structures have an identical configuration, in all cases similarly substituted, but nonetheless it appears in (**I**) and (**II**) with a different chirality than that ascribed to (**III**) and (**IV**). The answer comes from the way in which the chirality descriptor is obtained, according to the Cahn–Ingold–Prelog Rules (see, for instance, the 'Gold Book'; IUPAC, 1997), *e.g.* by considering the neighbourhood of the site. The fact that in (**III**) and (**IV**) atom C8 presents a bonded H atom where the other two, *i.e.* (**I**) and (**II**), have an O atom instead, reverses the priority assignments and thus, turns the assigned chirality from *R* to *S*. The puzzlement comes from matching (too loosely) the concept of 'similarity of a chirality sequence' to 'similarity of a structural configuration'. As shown in the preceding example, differences in the attached substituents can play unexpected tricks.

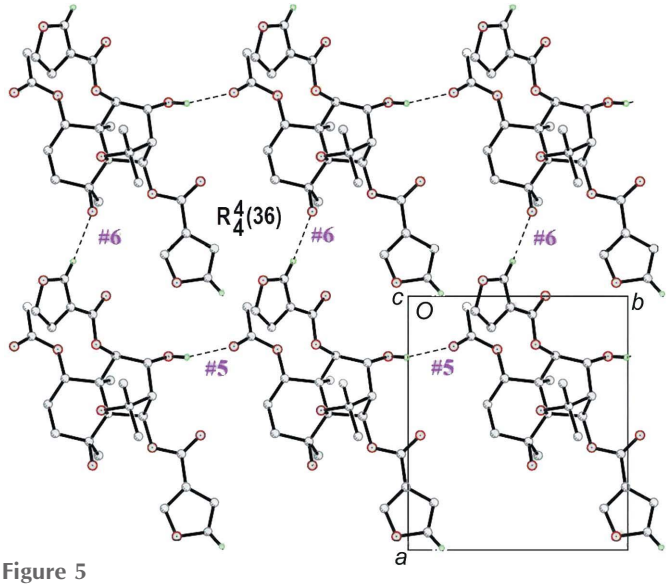


Figure 5
Packing diagram of (**II**).

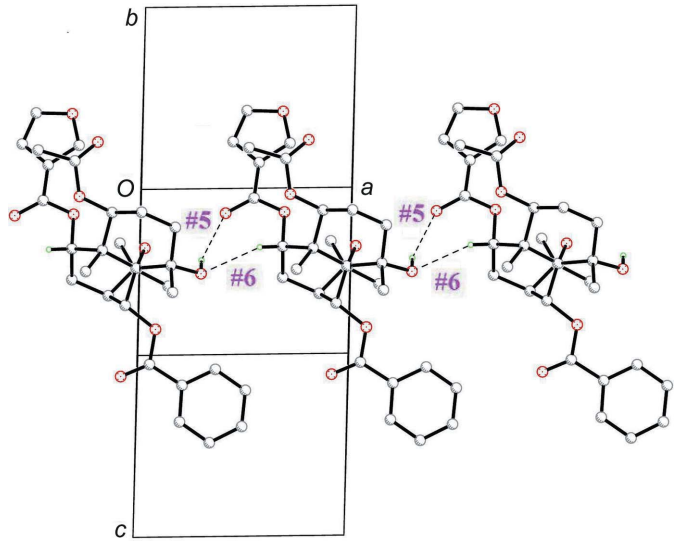


Figure 7
Packing diagram of (**IV**).

Regarding similarities, in all three compounds, the globular shape of the inner skeleton [see Figs. 2–4 for space-filling views of (**II**)–(**IV**)] is associated, either as the cause or eventually as the consequence, with a number of intramolecular hydrogen bonds, the most relevant of which are those labelled #1 to #4 in Table 2.

This very 'closeness', in turn, inhibits most of the inner potential acceptors (and some of the aforementioned strong donors), to enter into close contact with neighbouring molecules. In the case of the structural reference, (**I**), atom O1*A* (attached to C6) 'donates' one intramolecular hydrogen bond and 'accepts' two, thus precluding its participation in intermolecular contacts. In (**II**) and (**III**), this site (C6) is not substituted by a donor (since the OH group is replaced by a furoate group), but it is, in turn, O2 (attached to C4), with its H2 slightly rotated inwards, which internally 'donates' its hydrogen bond to the O1 atom nearby (see Figs. 2–4). As a consequence, the resulting availability of strong donors for the consolidation of the crystal structure, and the dimensionalities resulting from this fact, reduce sensibly when analyzing them in a (**I**)→(**IV**) order. [For packing diagrams for (**II**)–(**IV**), see Figs. 5–7.] Thus, the larger number corresponds to (**I**), with atoms O2 and O3 defining two families of chains to give rise to a final three-dimensional structure due to a cris-cross interconnection (discussed in the original paper), only one in (**II**) [atom O3, #5 for (**II**) in Table 2, giving rise to one single family of [010] chains, highlighted in Fig. 5], none in (**III**) (with isolated molecular fragments) and one in (**IV**) [atom O2, #5 for (**IV**) in Table 2, and Fig. 7], defining [100] chains. The stronger O—H···O and the weaker C—H···O interactions presented in Table 2 associate in (**II**) and (**III**) to define two-dimensional structures parallel to (001), made up of large macrocycles [$R_4^4(36)$ in (**II**) (Fig. 5) and $R_4^4(44)$ in (**III**) (Fig. 6); see Bernstein *et al.* (1995) for notation]. The inset in Fig. 6 provides a subtle example of the structural reorganization; the absence in (**III**) of the strong #5 hydrogen bond seen in (**II**) produces a slight realigment of neighbouring molecules, favouring the appearance of the (much weaker) #5 [for (**III**)] interaction, and thus promotes the reorganization of the macrocycle. In the case of (**IV**), these weaker C—H···O hydrogen bonds just serve to reinforce the cohesion of the [100] chain (Fig. 7).

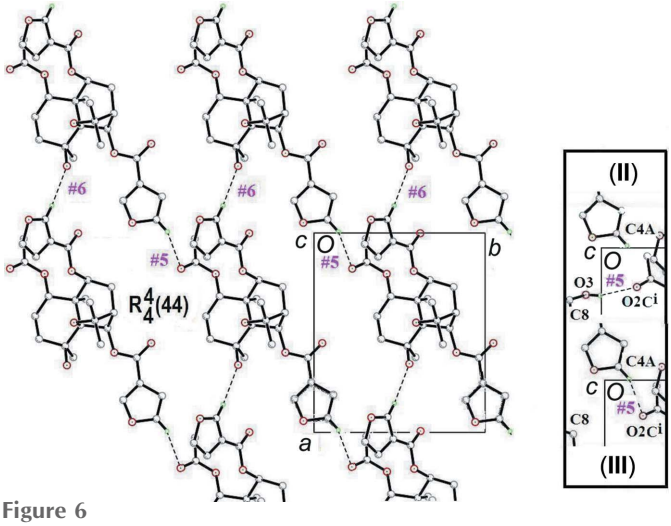


Figure 6
Packing diagram of (**III**). The inset provides an example of the structural reorganization.

Incidentally, in (**II**)–(**IV**), there is a clear correlation between the hydrogen-bonding interactions and the melting points of the compounds. Thus, structure (**III**), with no strong intermolecular hydrogen bonds, shows the lowest melting point, while among the remaining two structures, structure (**II**), with stronger O—H···O and C—H···O intermolecular hydrogen bonds, has the higher melting point.

Acknowledgements

NV thanks Conicet for a PhD fellowship. The authors gratefully acknowledge Dr Sebastián Suárez (INQUIMAE, FCEN–

UBA), for collection of the X-ray data and invaluable help in the AIM analysis calculations, and Dr Fabio Cukiernik (INQUIMAE, FCEN–UBA), for useful discussions.

Funding information

Funding for this research was provided by: University of La Frontera; Ministerio de Educación of Chile (Program MECE Superior Education); ANPCyT (project No. PME 2006–01113, for the purchase of the Oxford Gemini CCD diffractometer).

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supporting information

Acta Cryst. (2018). C**74**, 564-570 [https://doi.org/10.1107/S2053229618005429]

Three new dihydro-*β*-agarofuran sesquiterpenes from the seeds of *Maytenus boaria*

Cristian Paz, Matthias Heydenreich, Bernd Schmidt, Nahir Vadra and Ricardo Baggio

Computing details

For all structures, data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2009); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

(1*S*,4*S*,5*S*,6*R*,7*R*,8*R*,9*R*,10*S*)-6-Acetoxy-4,9-dihydroxy-2,2,5a,9-tetramethyloctahydro-2*H*-3,9a-methanobenzo[*b*]oxepine-5,10-diyl bis(furan-3-carboxylate) (II)

Crystal data

$C_{27}H_{32}O_{11}$
M_r = 532.52
Monoclinic, $P2_1$
a = 11.2664 (3) Å
b = 9.6575 (3) Å
c = 12.0758 (4) Å
β = 98.262 (3)°
V = 1300.28 (6) Å^3
Z = 2
$F(000)$ = 564
D_x = 1.360 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.7107 Å
Cell parameters from 2709 reflections
θ = 4.2–20.4°
μ = 0.11 mm^{-1}
T = 294 K
Block, colourless
0.28 × 0.18 × 0.14 mm

Data collection

CCD Oxford Diffraction Xcalibur, Eos, Gemini diffractometer
thick slices scans
Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009)
T_{min} = 0.95, T_{max} = 0.98
32072 measured reflections
5376 independent reflections
4132 reflections with $I > 2\sigma(I)$
R_{int} = 0.053
θ_{max} = 26.5°, θ_{min} = 3.8°
h = −14→14
k = −12→12
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.120
S = 0.96
5376 reflections
356 parameters
3 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0748P)^2 + 0.0201P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Absolute structure: Absolute structure assigned by comparison with related compounds of the same origin.

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.45046 (17)	0.6039 (2)	0.34735 (16)	0.0334 (5)
O2	0.6670 (2)	0.5638 (3)	0.2980 (2)	0.0499 (6)
H2	0.634 (3)	0.557 (5)	0.357 (2)	0.060*
O3	0.2374 (2)	0.9090 (3)	0.1659 (2)	0.0545 (7)
H3	0.239 (4)	0.990 (2)	0.194 (4)	0.065*
O1A	0.59613 (18)	0.8357 (2)	0.2523 (2)	0.0418 (5)
O2A	0.5480 (2)	1.0554 (3)	0.2082 (3)	0.0638 (8)
O1B	0.19077 (17)	0.5805 (2)	0.28708 (18)	0.0380 (5)
O2B	−0.0007 (2)	0.6249 (3)	0.2174 (3)	0.0800 (11)
O1C	0.2103 (2)	0.4054 (3)	0.0955 (2)	0.0517 (6)
O2C	0.1984 (3)	0.2083 (3)	0.1905 (3)	0.0734 (9)
C1	0.3244 (3)	0.4389 (3)	0.1630 (3)	0.0392 (7)
H1	0.320942	0.411590	0.240687	0.047*
C2	0.4263 (3)	0.3614 (3)	0.1210 (3)	0.0501 (9)
H2A	0.433815	0.390627	0.045456	0.060*
H2B	0.410725	0.262621	0.120163	0.060*
C3	0.5405 (3)	0.3936 (4)	0.1990 (3)	0.0481 (9)
H3A	0.606173	0.342888	0.174195	0.058*
H3B	0.532014	0.360960	0.273453	0.058*
C4	0.5725 (3)	0.5480 (3)	0.2055 (3)	0.0396 (7)
C5	0.4620 (3)	0.6349 (3)	0.2307 (3)	0.0313 (6)
C6	0.4723 (3)	0.7931 (3)	0.2263 (3)	0.0348 (7)
H6	0.437557	0.827560	0.152415	0.042*
C7	0.3935 (3)	0.8342 (3)	0.3142 (3)	0.0374 (7)
H7	0.408612	0.929997	0.338994	0.045*
C8	0.2632 (3)	0.8149 (3)	0.2566 (3)	0.0404 (8)
H8	0.208723	0.833577	0.311189	0.049*
C9	0.2347 (3)	0.6705 (3)	0.2053 (3)	0.0378 (7)
H9	0.169328	0.681945	0.143086	0.045*
C10	0.3393 (3)	0.5961 (3)	0.1582 (2)	0.0329 (6)
C11	0.4333 (3)	0.7309 (3)	0.4096 (3)	0.0375 (7)
C12	0.5521 (3)	0.7714 (4)	0.4810 (3)	0.0500 (9)
H12A	0.575543	0.700266	0.535334	0.075*
H12B	0.542126	0.857203	0.518665	0.075*
H12C	0.613095	0.781916	0.433658	0.075*
C13	0.3436 (3)	0.7035 (4)	0.4900 (3)	0.0500 (9)

H13A	0.268664	0.674376	0.448562	0.075*
H13B	0.331718	0.786692	0.530470	0.075*
H13C	0.373989	0.632033	0.541737	0.075*
C14	0.6270 (3)	0.5915 (4)	0.1023 (3)	0.0531 (9)
H14A	0.630732	0.690740	0.099054	0.080*
H14B	0.578035	0.557348	0.036262	0.080*
H14C	0.706356	0.553934	0.106463	0.080*
C15	0.3310 (3)	0.6448 (4)	0.0347 (3)	0.0452 (8)
H15A	0.405550	0.626044	0.007803	0.068*
H15B	0.315087	0.742435	0.030496	0.068*
H15C	0.267380	0.595966	−0.010421	0.068*
C1A	0.6222 (3)	0.9681 (3)	0.2339 (3)	0.0408 (8)
C2A	0.7521 (3)	0.9887 (4)	0.2479 (3)	0.0475 (8)
C3A	0.8141 (4)	1.1171 (5)	0.2624 (4)	0.0708 (12)
H3A1	0.779723	1.204158	0.266957	0.085*
C4A	0.9283 (4)	1.0899 (6)	0.2680 (4)	0.0828 (15)
H4A	0.989115	1.155694	0.277454	0.099*
O3A	0.9459 (3)	0.9473 (5)	0.2576 (4)	0.1034 (13)
C5A	0.8354 (4)	0.8903 (5)	0.2446 (4)	0.0724 (13)
H5A	0.819348	0.796261	0.234627	0.087*
C1B	0.0713 (3)	0.5645 (4)	0.2814 (3)	0.0421 (8)
C2B	0.0443 (3)	0.4647 (4)	0.3649 (3)	0.0439 (8)
C3B	0.1226 (4)	0.3784 (5)	0.4343 (4)	0.0637 (11)
H3B1	0.205316	0.374118	0.436409	0.076*
C4B	0.0591 (5)	0.3046 (5)	0.4960 (4)	0.0828 (16)
H4B	0.089763	0.238766	0.548658	0.099*
O3B	−0.0620 (3)	0.3407 (4)	0.4699 (3)	0.0945 (11)
C5B	−0.0669 (3)	0.4355 (5)	0.3889 (4)	0.0618 (11)
H5B	−0.137226	0.475996	0.353658	0.074*
C1C	0.1570 (4)	0.2864 (4)	0.1177 (4)	0.0579 (10)
C2C	0.0417 (5)	0.2669 (7)	0.0407 (4)	0.100 (2)
H2C1	0.018985	0.171030	0.040006	0.150*
H2C2	0.051981	0.295148	−0.033493	0.150*
H2C3	−0.019903	0.321947	0.066362	0.150*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0370 (11)	0.0319 (10)	0.0314 (11)	−0.0009 (9)	0.0057 (8)	0.0016 (9)
O2	0.0388 (13)	0.0532 (14)	0.0571 (16)	0.0075 (11)	0.0047 (11)	0.0050 (12)
O3	0.0593 (15)	0.0332 (12)	0.0689 (17)	0.0090 (12)	0.0019 (13)	0.0091 (12)
O1A	0.0342 (12)	0.0332 (12)	0.0577 (15)	−0.0069 (9)	0.0058 (10)	0.0031 (10)
O2A	0.0524 (16)	0.0354 (13)	0.101 (2)	−0.0025 (12)	0.0037 (14)	0.0143 (14)
O1B	0.0295 (11)	0.0399 (12)	0.0437 (12)	−0.0046 (9)	0.0017 (9)	0.0059 (10)
O2B	0.0340 (14)	0.098 (2)	0.106 (3)	0.0133 (15)	0.0024 (15)	0.050 (2)
O1C	0.0589 (15)	0.0429 (13)	0.0503 (14)	−0.0162 (12)	−0.0028 (11)	−0.0028 (11)
O2C	0.094 (2)	0.0451 (15)	0.081 (2)	−0.0225 (15)	0.0138 (18)	0.0006 (16)
C1	0.0467 (19)	0.0296 (16)	0.0397 (17)	−0.0070 (13)	0.0006 (14)	−0.0025 (13)

C2	0.070 (2)	0.0316 (17)	0.051 (2)	0.0025 (16)	0.0168 (18)	−0.0078 (15)
C3	0.055 (2)	0.0353 (17)	0.056 (2)	0.0097 (16)	0.0157 (18)	0.0024 (15)
C4	0.0410 (17)	0.0358 (16)	0.0431 (18)	0.0074 (14)	0.0101 (14)	0.0031 (14)
C5	0.0345 (15)	0.0285 (15)	0.0316 (16)	−0.0001 (12)	0.0068 (12)	0.0009 (12)
C6	0.0303 (15)	0.0296 (15)	0.0441 (18)	−0.0022 (12)	0.0044 (13)	0.0011 (13)
C7	0.0355 (17)	0.0282 (15)	0.0487 (19)	−0.0038 (13)	0.0071 (14)	−0.0059 (14)
C8	0.0360 (17)	0.0314 (16)	0.054 (2)	0.0040 (13)	0.0067 (14)	0.0014 (14)
C9	0.0341 (16)	0.0365 (17)	0.0410 (18)	−0.0024 (13)	−0.0004 (13)	0.0058 (13)
C10	0.0382 (16)	0.0274 (15)	0.0329 (16)	−0.0015 (13)	0.0046 (12)	−0.0009 (13)
C11	0.0348 (17)	0.0374 (17)	0.0402 (18)	−0.0021 (13)	0.0049 (13)	−0.0083 (14)
C12	0.048 (2)	0.059 (2)	0.0407 (19)	−0.0083 (16)	0.0004 (15)	−0.0101 (16)
C13	0.050 (2)	0.059 (2)	0.043 (2)	−0.0051 (17)	0.0124 (16)	−0.0085 (17)
C14	0.055 (2)	0.051 (2)	0.058 (2)	0.0070 (17)	0.0252 (17)	0.0043 (18)
C15	0.058 (2)	0.0423 (19)	0.0333 (18)	−0.0036 (16)	0.0001 (15)	0.0053 (14)
C1A	0.0453 (19)	0.0370 (18)	0.0405 (18)	−0.0096 (15)	0.0069 (14)	0.0008 (14)
C2A	0.0435 (19)	0.055 (2)	0.0450 (19)	−0.0119 (17)	0.0097 (15)	0.0022 (16)
C3A	0.065 (3)	0.065 (3)	0.080 (3)	−0.026 (2)	0.004 (2)	0.005 (2)
C4A	0.060 (3)	0.093 (4)	0.097 (4)	−0.042 (3)	0.018 (2)	−0.008 (3)
O3A	0.0449 (18)	0.133 (4)	0.134 (3)	−0.015 (2)	0.0189 (18)	−0.019 (3)
C5A	0.044 (2)	0.070 (3)	0.103 (4)	−0.010 (2)	0.009 (2)	−0.010 (3)
C1B	0.0313 (17)	0.0405 (18)	0.054 (2)	0.0020 (14)	0.0041 (14)	−0.0001 (16)
C2B	0.0353 (17)	0.0445 (19)	0.052 (2)	−0.0061 (14)	0.0074 (15)	−0.0041 (15)
C3B	0.048 (2)	0.070 (3)	0.070 (3)	−0.0044 (19)	−0.0008 (19)	0.026 (2)
C4B	0.078 (3)	0.089 (4)	0.078 (3)	−0.018 (3)	−0.002 (3)	0.042 (3)
O3B	0.084 (3)	0.105 (3)	0.099 (3)	−0.034 (2)	0.030 (2)	0.014 (2)
C5B	0.043 (2)	0.068 (3)	0.077 (3)	−0.0085 (19)	0.0146 (19)	0.002 (2)
C1C	0.071 (3)	0.048 (2)	0.055 (2)	−0.022 (2)	0.009 (2)	−0.0141 (19)
C2C	0.100 (4)	0.117 (5)	0.076 (3)	−0.065 (4)	−0.010 (3)	−0.006 (3)

Geometric parameters (Å, º)

O1—C5	1.464 (4)	C10—C15	1.554 (4)
O1—C11	1.466 (4)	C11—C13	1.521 (5)
O2—C4	1.437 (4)	C11—C12	1.535 (4)
O2—H2	0.852 (14)	C12—H12A	0.9600
O3—C8	1.421 (4)	C12—H12B	0.9600
O3—H3	0.851 (14)	C12—H12C	0.9600
O1A—C1A	1.338 (4)	C13—H13A	0.9600
O1A—C6	1.445 (4)	C13—H13B	0.9600
O2A—C1A	1.197 (4)	C13—H13C	0.9600
O1B—C1B	1.347 (4)	C14—H14A	0.9600
O1B—C9	1.454 (4)	C14—H14B	0.9600
O2B—C1B	1.190 (4)	C14—H14C	0.9600
O1C—C1C	1.342 (5)	C15—H15A	0.9600
O1C—C1	1.456 (4)	C15—H15B	0.9600
O2C—C1C	1.201 (5)	C15—H15C	0.9600
C1—C2	1.518 (5)	C1A—C2A	1.462 (5)
C1—C10	1.530 (4)	C2A—C5A	1.341 (6)

C1—H1	0.9800	C2A—C3A	1.422 (6)
C2—C3	1.514 (5)	C3A—C4A	1.306 (6)
C2—H2A	0.9700	C3A—H3A1	0.9300
C2—H2B	0.9700	C4A—O3A	1.399 (8)
C3—C4	1.534 (5)	C4A—H4A	0.9300
C3—H3A	0.9700	O3A—C5A	1.350 (5)
C3—H3B	0.9700	C5A—H5A	0.9300
C4—C14	1.526 (5)	C1B—C2B	1.458 (5)
C4—C5	1.567 (4)	C2B—C5B	1.356 (5)
C5—C6	1.533 (4)	C2B—C3B	1.400 (5)
C5—C10	1.572 (4)	C3B—C4B	1.315 (6)
C6—C7	1.531 (5)	C3B—H3B1	0.9300
C6—H6	0.9800	C4B—O3B	1.399 (6)
C7—C11	1.541 (5)	C4B—H4B	0.9300
C7—C8	1.543 (4)	O3B—C5B	1.334 (6)
C7—H7	0.9800	C5B—H5B	0.9300
C8—C9	1.541 (5)	C1C—C2C	1.496 (6)
C8—H8	0.9800	C2C—H2C1	0.9600
C9—C10	1.556 (4)	C2C—H2C2	0.9600
C9—H9	0.9800	C2C—H2C3	0.9600

C5—O1—C11	111.0 (2)	O1—C11—C7	101.8 (2)
C4—O2—H2	106 (3)	C13—C11—C7	116.2 (3)
C8—O3—H3	107 (3)	C12—C11—C7	113.1 (3)
C1A—O1A—C6	117.7 (2)	C11—C12—H12A	109.5
C1B—O1B—C9	118.0 (2)	C11—C12—H12B	109.5
C1C—O1C—C1	117.6 (3)	H12A—C12—H12B	109.5
O1C—C1—C2	110.6 (3)	C11—C12—H12C	109.5
O1C—C1—C10	107.0 (2)	H12A—C12—H12C	109.5
C2—C1—C10	112.6 (3)	H12B—C12—H12C	109.5
O1C—C1—H1	108.9	C11—C13—H13A	109.5
C2—C1—H1	108.9	C11—C13—H13B	109.5
C10—C1—H1	108.9	H13A—C13—H13B	109.5
C1—C2—C3	107.9 (3)	C11—C13—H13C	109.5
C1—C2—H2A	110.1	H13A—C13—H13C	109.5
C3—C2—H2A	110.1	H13B—C13—H13C	109.5
C1—C2—H2B	110.1	C4—C14—H14A	109.5
C3—C2—H2B	110.1	C4—C14—H14B	109.5
H2A—C2—H2B	108.4	H14A—C14—H14B	109.5
C2—C3—C4	113.8 (3)	C4—C14—H14C	109.5
C2—C3—H3A	108.8	H14A—C14—H14C	109.5
C4—C3—H3A	108.8	H14B—C14—H14C	109.5
C2—C3—H3B	108.8	C10—C15—H15A	109.5
C4—C3—H3B	108.8	C10—C15—H15B	109.5
H3A—C3—H3B	107.7	H15A—C15—H15B	109.5
O2—C4—C14	105.4 (3)	C10—C15—H15C	109.5
O2—C4—C3	106.6 (3)	H15A—C15—H15C	109.5
C14—C4—C3	110.2 (3)	H15B—C15—H15C	109.5

O2—C4—C5	108.2 (3)	O2A—C1A—O1A	123.7 (3)
C14—C4—C5	115.8 (3)	O2A—C1A—C2A	125.7 (3)
C3—C4—C5	110.1 (3)	O1A—C1A—C2A	110.6 (3)
O1—C5—C6	104.8 (2)	C5A—C2A—C3A	106.8 (4)
O1—C5—C4	105.1 (2)	C5A—C2A—C1A	126.4 (4)
C6—C5—C4	117.4 (3)	C3A—C2A—C1A	126.8 (4)
O1—C5—C10	107.1 (2)	C4A—C3A—C2A	107.0 (4)
C6—C5—C10	106.4 (2)	C4A—C3A—H3A1	126.5
C4—C5—C10	115.1 (2)	C2A—C3A—H3A1	126.5
O1A—C6—C7	114.5 (3)	C3A—C4A—O3A	110.2 (4)
O1A—C6—C5	110.6 (2)	C3A—C4A—H4A	124.9
C7—C6—C5	100.4 (2)	O3A—C4A—H4A	124.9
O1A—C6—H6	110.4	C5A—O3A—C4A	105.7 (4)
C7—C6—H6	110.4	C2A—C5A—O3A	110.2 (4)
C5—C6—H6	110.4	C2A—C5A—H5A	124.9
C6—C7—C11	102.4 (2)	O3A—C5A—H5A	124.9
C6—C7—C8	105.4 (3)	O2B—C1B—O1B	124.0 (3)
C11—C7—C8	114.5 (3)	O2B—C1B—C2B	125.7 (3)
C6—C7—H7	111.3	O1B—C1B—C2B	110.3 (3)
C11—C7—H7	111.3	C5B—C2B—C3B	105.6 (4)
C8—C7—H7	111.3	C5B—C2B—C1B	125.2 (3)
O3—C8—C9	105.2 (3)	C3B—C2B—C1B	129.1 (3)
O3—C8—C7	110.3 (3)	C4B—C3B—C2B	108.4 (4)
C9—C8—C7	114.9 (3)	C4B—C3B—H3B1	125.8
O3—C8—H8	108.8	C2B—C3B—H3B1	125.8
C9—C8—H8	108.8	C3B—C4B—O3B	109.2 (4)
C7—C8—H8	108.8	C3B—C4B—H4B	125.4
O1B—C9—C8	109.9 (3)	O3B—C4B—H4B	125.4
O1B—C9—C10	108.8 (2)	C5B—O3B—C4B	105.8 (3)
C8—C9—C10	116.1 (3)	O3B—C5B—C2B	110.9 (4)
O1B—C9—H9	107.3	O3B—C5B—H5B	124.5
C8—C9—H9	107.3	C2B—C5B—H5B	124.5
C10—C9—H9	107.3	O2C—C1C—O1C	123.1 (4)
C1—C10—C15	110.2 (3)	O2C—C1C—C2C	126.0 (4)
C1—C10—C9	110.6 (3)	O1C—C1C—C2C	111.0 (4)
C15—C10—C9	105.5 (3)	C1C—C2C—H2C1	109.5
C1—C10—C5	108.0 (2)	C1C—C2C—H2C2	109.5
C15—C10—C5	112.9 (2)	H2C1—C2C—H2C2	109.5
C9—C10—C5	109.8 (2)	C1C—C2C—H2C3	109.5
O1—C11—C13	109.3 (3)	H2C1—C2C—H2C3	109.5
O1—C11—C12	109.4 (2)	H2C2—C2C—H2C3	109.5
C13—C11—C12	106.9 (3)		

(1*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-6-Acetoxy-9-hydroxy-2,2,5a,9-tetramethyloctahydro-2*H*-3,9a-methanobenzo[*b*]oxepine-5,10-diyl bis(furan-3-carboxylate) (III)

Crystal data

$C_{27}H_{32}O_{10}$
$M_r = 516.52$
Monoclinic, $P2_1$
$a = 11.2999$ (3) Å
$b = 9.6363$ (3) Å
$c = 12.1306$ (4) Å
$\beta = 97.539$ (3)°
$V = 1309.47$ (7) Å^3
$Z = 2$
$F(000) = 548$
$D_x = 1.310$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8169 reflections
$\theta = 4.0$–$23.4°$
$\mu = 0.10$ mm^{-1}
$T = 294$ K
Block, colourless
0.42 × 0.22 × 0.12 mm

Data collection

CCD Oxford Diffraction Xcalibur, Eos, Gemini diffractometer
Radiation source: Enhance (Mo) X-ray Source
thick slices scans
Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009)
$T_{min} = 0.95$, $T_{max} = 0.98$
29871 measured reflections
4858 independent reflections
4065 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$
$\theta_{max} = 25.5°$, $\theta_{min} = 3.6°$
$h = -13 \rightarrow 13$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.091$
$S = 1.07$
4858 reflections
343 parameters
2 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + 0.0872P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.13$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Absolute structure: Absolute structure assigned by comparison with related compounds of the same origin.

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.44939 (14)	0.59663 (18)	0.34937 (13)	0.0366 (4)
O2	0.66369 (17)	0.5550 (2)	0.29462 (17)	0.0523 (5)
H2	0.631 (3)	0.556 (4)	0.3545 (17)	0.063*
O1A	0.59914 (15)	0.83361 (19)	0.26145 (16)	0.0450 (5)
O2A	0.5524 (2)	1.0489 (2)	0.2004 (2)	0.0673 (6)
O1B	0.19019 (15)	0.5841 (2)	0.29323 (15)	0.0477 (5)
O2B	0.00065 (19)	0.6212 (3)	0.2181 (2)	0.0836 (9)
O1C	0.2049 (2)	0.4249 (3)	0.08952 (18)	0.0681 (7)

O2C	0.1788 (3)	0.2253 (4)	0.1761 (3)	0.1038 (10)
C1	0.3179 (3)	0.4480 (3)	0.1586 (2)	0.0496 (7)
H1	0.311296	0.414926	0.233981	0.060*
C2	0.4175 (3)	0.3695 (3)	0.1145 (3)	0.0613 (9)
H2A	0.426643	0.401991	0.040366	0.074*
H2B	0.399057	0.271202	0.110328	0.074*
C3	0.5314 (3)	0.3937 (3)	0.1922 (3)	0.0539 (8)
H3A	0.595370	0.342033	0.165060	0.065*
H3B	0.521486	0.357345	0.264939	0.065*
C4	0.5680 (2)	0.5456 (3)	0.2043 (2)	0.0434 (7)
C5	0.4615 (2)	0.6353 (3)	0.2350 (2)	0.0343 (6)
C6	0.4755 (2)	0.7933 (3)	0.2379 (2)	0.0389 (6)
H6	0.440045	0.833271	0.166895	0.047*
C7	0.3994 (2)	0.8292 (3)	0.3287 (2)	0.0461 (7)
H7	0.416886	0.923080	0.357333	0.055*
C8	0.2696 (2)	0.8175 (3)	0.2733 (3)	0.0524 (8)
H8A	0.254683	0.891197	0.218726	0.063*
H8B	0.217334	0.832854	0.329435	0.063*
C9	0.2358 (2)	0.6784 (3)	0.2153 (2)	0.0463 (7)
H9	0.170725	0.696706	0.155345	0.056*
C10	0.3378 (2)	0.6053 (3)	0.1627 (2)	0.0395 (6)
C11	0.4380 (2)	0.7200 (3)	0.4177 (2)	0.0424 (6)
C12	0.5575 (3)	0.7521 (4)	0.4876 (2)	0.0556 (8)
H12A	0.579446	0.676583	0.537699	0.083*
H12B	0.550462	0.835624	0.529341	0.083*
H12C	0.617784	0.764291	0.439461	0.083*
C13	0.3486 (3)	0.6894 (4)	0.4988 (3)	0.0594 (9)
H13A	0.273121	0.664284	0.457835	0.089*
H13B	0.338827	0.770524	0.542658	0.089*
H13C	0.377655	0.614229	0.546777	0.089*
C14	0.6230 (3)	0.5944 (4)	0.1019 (3)	0.0585 (8)
H14A	0.629535	0.693740	0.102916	0.088*
H14B	0.573026	0.565777	0.035636	0.088*
H14C	0.700903	0.554230	0.102953	0.088*
C15	0.3308 (3)	0.6638 (4)	0.0428 (2)	0.0576 (8)
H15A	0.404958	0.646725	0.014479	0.086*
H15B	0.316131	0.761860	0.043713	0.086*
H15C	0.267094	0.618870	−0.004092	0.086*
C1A	0.6263 (3)	0.9637 (3)	0.2333 (2)	0.0438 (7)
C2A	0.7548 (3)	0.9829 (3)	0.2451 (2)	0.0494 (7)
C3A	0.8184 (4)	1.1109 (4)	0.2486 (3)	0.0764 (11)
H3A1	0.785810	1.199663	0.245904	0.092*
C4A	0.9325 (4)	1.0788 (5)	0.2562 (3)	0.0888 (14)
H4A	0.994105	1.143345	0.260146	0.107*
O3A	0.9484 (2)	0.9377 (4)	0.2576 (3)	0.0988 (10)
C5A	0.8378 (3)	0.8840 (4)	0.2511 (3)	0.0744 (11)
H5A	0.821370	0.789451	0.250817	0.089*
C1B	0.0716 (2)	0.5632 (3)	0.2841 (3)	0.0490 (7)

C2B	0.0425 (2)	0.4605 (3)	0.3648 (3)	0.0487 (7)
C3B	0.1186 (3)	0.3748 (5)	0.4341 (3)	0.0768 (11)
H3B1	0.201450	0.374010	0.438920	0.092*
C4B	0.0556 (4)	0.2963 (5)	0.4907 (3)	0.0936 (15)
H4B	0.085303	0.227647	0.540671	0.112*
O3B	−0.0663 (3)	0.3326 (4)	0.4636 (3)	0.1098 (11)
C5B	−0.0690 (3)	0.4290 (4)	0.3862 (3)	0.0703 (10)
H5B	−0.138336	0.469995	0.350889	0.084*
C1C	0.1440 (4)	0.3079 (5)	0.1076 (3)	0.0799 (12)
C2C	0.0282 (5)	0.3032 (7)	0.0312 (4)	0.126 (2)
H2C1	0.002485	0.208623	0.020853	0.189*
H2C2	0.039296	0.342774	−0.039373	0.189*
H2C3	−0.031185	0.355289	0.063216	0.189*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0391 (9)	0.0379 (10)	0.0330 (9)	−0.0035 (8)	0.0062 (7)	0.0008 (8)
O2	0.0388 (11)	0.0600 (13)	0.0581 (13)	0.0073 (9)	0.0070 (9)	0.0062 (11)
O1A	0.0358 (10)	0.0377 (11)	0.0608 (12)	−0.0084 (8)	0.0034 (8)	0.0083 (9)
O2A	0.0607 (14)	0.0388 (12)	0.0999 (18)	−0.0041 (11)	0.0014 (12)	0.0132 (12)
O1B	0.0306 (9)	0.0622 (13)	0.0496 (11)	−0.0050 (9)	0.0022 (8)	0.0124 (10)
O2B	0.0355 (12)	0.097 (2)	0.116 (2)	0.0060 (13)	0.0000 (13)	0.0438 (18)
O1C	0.0699 (14)	0.0768 (16)	0.0550 (13)	−0.0363 (13)	−0.0021 (11)	−0.0053 (12)
O2C	0.108 (2)	0.093 (2)	0.110 (2)	−0.0574 (19)	0.0115 (19)	0.011 (2)
C1	0.0559 (18)	0.0509 (18)	0.0418 (16)	−0.0184 (15)	0.0054 (13)	−0.0041 (13)
C2	0.086 (2)	0.0470 (18)	0.0556 (19)	−0.0142 (17)	0.0262 (18)	−0.0114 (15)
C3	0.068 (2)	0.0362 (16)	0.061 (2)	0.0054 (15)	0.0238 (17)	−0.0016 (14)
C4	0.0452 (16)	0.0429 (16)	0.0439 (15)	0.0038 (13)	0.0133 (12)	0.0023 (13)
C5	0.0357 (13)	0.0342 (14)	0.0334 (14)	−0.0056 (11)	0.0069 (11)	0.0043 (11)
C6	0.0306 (13)	0.0370 (15)	0.0478 (15)	−0.0037 (11)	0.0006 (11)	0.0051 (12)
C7	0.0418 (15)	0.0381 (15)	0.0587 (18)	−0.0012 (12)	0.0077 (13)	−0.0091 (13)
C8	0.0408 (15)	0.0463 (17)	0.071 (2)	0.0082 (13)	0.0089 (14)	0.0076 (15)
C9	0.0343 (14)	0.0539 (18)	0.0490 (17)	−0.0026 (12)	−0.0010 (12)	0.0140 (14)
C10	0.0388 (14)	0.0443 (16)	0.0350 (14)	−0.0080 (12)	0.0033 (11)	0.0045 (12)
C11	0.0412 (15)	0.0447 (16)	0.0418 (15)	−0.0028 (13)	0.0076 (12)	−0.0074 (13)
C12	0.0524 (18)	0.064 (2)	0.0486 (18)	−0.0130 (16)	0.0012 (14)	−0.0088 (16)
C13	0.0549 (19)	0.078 (2)	0.0477 (18)	−0.0073 (16)	0.0154 (15)	−0.0094 (16)
C14	0.0595 (18)	0.062 (2)	0.0595 (19)	0.0003 (16)	0.0272 (15)	0.0054 (17)
C15	0.0602 (19)	0.070 (2)	0.0402 (17)	−0.0147 (16)	−0.0019 (14)	0.0131 (15)
C1A	0.0503 (17)	0.0384 (16)	0.0430 (15)	−0.0112 (14)	0.0079 (13)	0.0004 (13)
C2A	0.0496 (17)	0.0528 (19)	0.0463 (16)	−0.0161 (15)	0.0088 (13)	0.0013 (14)
C3A	0.074 (3)	0.068 (2)	0.084 (3)	−0.033 (2)	−0.0007 (19)	0.008 (2)
C4A	0.070 (3)	0.105 (4)	0.092 (3)	−0.048 (3)	0.011 (2)	0.007 (3)
O3A	0.0479 (15)	0.115 (3)	0.135 (3)	−0.0221 (16)	0.0191 (16)	−0.010 (2)
C5A	0.0453 (19)	0.071 (3)	0.108 (3)	−0.0168 (19)	0.0126 (19)	−0.005 (2)
C1B	0.0278 (14)	0.0575 (19)	0.0611 (18)	−0.0008 (13)	0.0038 (13)	−0.0020 (16)
C2B	0.0339 (15)	0.0585 (19)	0.0545 (17)	−0.0070 (14)	0.0093 (13)	−0.0021 (15)

C3B	0.0507 (19)	0.101 (3)	0.077 (2)	−0.011 (2)	0.0018 (17)	0.032 (2)
C4B	0.085 (3)	0.115 (4)	0.077 (3)	−0.029 (3)	−0.004 (2)	0.045 (3)
O3B	0.103 (3)	0.133 (3)	0.100 (2)	−0.047 (2)	0.0371 (19)	0.012 (2)
C5B	0.0440 (18)	0.085 (3)	0.085 (3)	−0.0101 (17)	0.0181 (18)	−0.005 (2)
C1C	0.086 (3)	0.091 (3)	0.064 (2)	−0.048 (2)	0.013 (2)	−0.017 (2)
C2C	0.115 (4)	0.176 (6)	0.082 (3)	−0.094 (4)	−0.011 (3)	−0.011 (3)

Geometric parameters (Å, º)

O1—C5	1.460 (3)	C11—C13	1.528 (4)
O1—C11	1.465 (3)	C11—C12	1.529 (4)
O2—C4	1.437 (4)	C12—H12A	0.9600
O2—H2	0.856 (13)	C12—H12B	0.9600
O1A—C1A	1.346 (3)	C12—H12C	0.9600
O1A—C6	1.442 (3)	C13—H13A	0.9600
O2A—C1A	1.201 (4)	C13—H13B	0.9600
O1B—C1B	1.345 (3)	C13—H13C	0.9600
O1B—C9	1.453 (3)	C14—H14A	0.9600
O2B—C1B	1.195 (4)	C14—H14B	0.9600
O1C—C1C	1.354 (5)	C14—H14C	0.9600
O1C—C1	1.450 (4)	C15—H15A	0.9600
O2C—C1C	1.180 (5)	C15—H15B	0.9600
C1—C2	1.510 (4)	C15—H15C	0.9600
C1—C10	1.533 (4)	C1A—C2A	1.452 (4)
C1—H1	0.9800	C2A—C5A	1.333 (5)
C2—C3	1.511 (5)	C2A—C3A	1.426 (5)
C2—H2A	0.9700	C3A—C4A	1.317 (6)
C2—H2B	0.9700	C3A—H3A1	0.9300
C3—C4	1.523 (4)	C4A—O3A	1.371 (6)
C3—H3A	0.9700	C4A—H4A	0.9300
C3—H3B	0.9700	O3A—C5A	1.345 (4)
C4—C14	1.535 (4)	C5A—H5A	0.9300
C4—C5	1.566 (4)	C1B—C2B	1.460 (4)
C5—C6	1.530 (4)	C2B—C5B	1.354 (4)
C5—C10	1.576 (3)	C2B—C3B	1.392 (5)
C6—C7	1.523 (4)	C3B—C4B	1.296 (5)
C6—H6	0.9800	C3B—H3B1	0.9300
C7—C11	1.529 (4)	C4B—O3B	1.417 (5)
C7—C8	1.535 (4)	C4B—H4B	0.9300
C7—H7	0.9800	O3B—C5B	1.318 (5)
C8—C9	1.538 (4)	C5B—H5B	0.9300
C8—H8A	0.9700	C1C—C2C	1.501 (6)
C8—H8B	0.9700	C2C—H2C1	0.9600
C9—C10	1.558 (4)	C2C—H2C2	0.9600
C9—H9	0.9800	C2C—H2C3	0.9600
C10—C15	1.553 (4)		
C5—O1—C11	110.90 (19)	O1—C11—C7	101.3 (2)

C4—O2—H2	107 (2)	C13—C11—C7	115.8 (2)
C1A—O1A—C6	116.6 (2)	C12—C11—C7	113.7 (2)
C1B—O1B—C9	118.3 (2)	C11—C12—H12A	109.5
C1C—O1C—C1	117.5 (3)	C11—C12—H12B	109.5
O1C—C1—C2	111.0 (2)	H12A—C12—H12B	109.5
O1C—C1—C10	106.5 (2)	C11—C12—H12C	109.5
C2—C1—C10	113.2 (2)	H12A—C12—H12C	109.5
O1C—C1—H1	108.7	H12B—C12—H12C	109.5
C2—C1—H1	108.7	C11—C13—H13A	109.5
C10—C1—H1	108.7	C11—C13—H13B	109.5
C1—C2—C3	108.3 (2)	H13A—C13—H13B	109.5
C1—C2—H2A	110.0	C11—C13—H13C	109.5
C3—C2—H2A	110.0	H13A—C13—H13C	109.5
C1—C2—H2B	110.0	H13B—C13—H13C	109.5
C3—C2—H2B	110.0	C4—C14—H14A	109.5
H2A—C2—H2B	108.4	C4—C14—H14B	109.5
C2—C3—C4	114.0 (3)	H14A—C14—H14B	109.5
C2—C3—H3A	108.7	C4—C14—H14C	109.5
C4—C3—H3A	108.7	H14A—C14—H14C	109.5
C2—C3—H3B	108.7	H14B—C14—H14C	109.5
C4—C3—H3B	108.7	C10—C15—H15A	109.5
H3A—C3—H3B	107.6	C10—C15—H15B	109.5
O2—C4—C3	107.6 (2)	H15A—C15—H15B	109.5
O2—C4—C14	104.7 (2)	C10—C15—H15C	109.5
C3—C4—C14	110.5 (3)	H15A—C15—H15C	109.5
O2—C4—C5	108.0 (2)	H15B—C15—H15C	109.5
C3—C4—C5	110.3 (2)	O2A—C1A—O1A	123.3 (3)
C14—C4—C5	115.4 (2)	O2A—C1A—C2A	126.1 (3)
O1—C5—C6	104.7 (2)	O1A—C1A—C2A	110.6 (3)
O1—C5—C4	104.82 (19)	C5A—C2A—C3A	105.6 (3)
C6—C5—C4	118.3 (2)	C5A—C2A—C1A	127.0 (3)
O1—C5—C10	107.17 (17)	C3A—C2A—C1A	127.4 (3)
C6—C5—C10	106.0 (2)	C4A—C3A—C2A	106.5 (4)
C4—C5—C10	114.8 (2)	C4A—C3A—H3A1	126.7
O1A—C6—C7	114.8 (2)	C2A—C3A—H3A1	126.7
O1A—C6—C5	111.5 (2)	C3A—C4A—O3A	111.0 (3)
C7—C6—C5	100.1 (2)	C3A—C4A—H4A	124.5
O1A—C6—H6	110.0	O3A—C4A—H4A	124.5
C7—C6—H6	110.0	C5A—O3A—C4A	105.2 (3)
C5—C6—H6	110.0	C2A—C5A—O3A	111.7 (3)
C6—C7—C11	102.6 (2)	C2A—C5A—H5A	124.2
C6—C7—C8	105.3 (2)	O3A—C5A—H5A	124.2
C11—C7—C8	115.3 (2)	O2B—C1B—O1B	124.0 (3)
C6—C7—H7	111.1	O2B—C1B—C2B	125.1 (3)
C11—C7—H7	111.1	O1B—C1B—C2B	110.9 (2)
C8—C7—H7	111.1	C5B—C2B—C3B	105.6 (3)
C7—C8—C9	115.5 (2)	C5B—C2B—C1B	125.3 (3)
C7—C8—H8A	108.4	C3B—C2B—C1B	129.1 (3)

C9—C8—H8A	108.4	C4B—C3B—C2B	109.1 (3)
C7—C8—H8B	108.4	C4B—C3B—H3B1	125.5
C9—C8—H8B	108.4	C2B—C3B—H3B1	125.5
H8A—C8—H8B	107.5	C3B—C4B—O3B	108.5 (4)
O1B—C9—C8	109.7 (2)	C3B—C4B—H4B	125.7
O1B—C9—C10	109.1 (2)	O3B—C4B—H4B	125.7
C8—C9—C10	115.3 (2)	C5B—O3B—C4B	105.7 (3)
O1B—C9—H9	107.5	O3B—C5B—C2B	111.0 (4)
C8—C9—H9	107.5	O3B—C5B—H5B	124.5
C10—C9—H9	107.5	C2B—C5B—H5B	124.5
C1—C10—C15	109.8 (2)	O2C—C1C—O1C	123.1 (4)
C1—C10—C9	110.3 (2)	O2C—C1C—C2C	126.7 (4)
C15—C10—C9	105.7 (2)	O1C—C1C—C2C	110.2 (4)
C1—C10—C5	108.3 (2)	C1C—C2C—H2C1	109.5
C15—C10—C5	112.8 (2)	C1C—C2C—H2C2	109.5
C9—C10—C5	109.8 (2)	H2C1—C2C—H2C2	109.5
O1—C11—C13	108.8 (2)	C1C—C2C—H2C3	109.5
O1—C11—C12	109.9 (2)	H2C1—C2C—H2C3	109.5
C13—C11—C12	107.1 (2)	H2C2—C2C—H2C3	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1	0.86 (1)	2.08 (3)	2.625 (2)	120 (3)
C12—H12*C*···O1*A*	0.96	2.24	2.949 (4)	130
C13—H13*A*···O1*B*	0.96	2.23	3.047 (4)	142
C14—H14*A*···O1*A*	0.96	2.41	3.045 (4)	123
C4*A*—H4*A*···O2*C*^{i}	0.93	2.56	3.375 (5)	146
C5*B*—H5*B*···O2^{ii}	0.93	2.40	3.309 (4)	167

Symmetry codes: (i) *x*+1, *y*+1, *z*; (ii) *x*−1, *y*, *z*.

(1*S*,4*S*,5*S*,6*R*,7*R*,9*S*,10*S*)-\ 6-Acetoxy-10-(benzoyloxy)-9-hydroxy-2,2,5a,9-tetramethyloctahydro-2*H*-\ 3,9a-methanobenzo[*b*]oxepin-5-yl furan-3-carboxylate (IV)

Crystal data

$C_{29}H_{34}O_9$
M_r = 526.56
Monoclinic, $P2_1$
a = 7.9045 (4) Å
b = 9.2038 (5) Å
c = 19.3935 (9) Å
β = 93.073 (4)°
V = 1408.88 (12) Å^3
Z = 2

F(000) = 560
D_x = 1.241 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 2709 reflections
θ = 4.2–20.4°
μ = 0.09 mm^{-1}
T = 294 K
Blocks, colourless
0.50 × 0.23 × 0.20 mm

Data collection

CCD Oxford Diffraction Xcalibur, Eos, Gemini diffractometer
Radiation source: Enhance (Mo) X-ray Source

thick slices scans
Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009)

T_{min} = 0.96, T_{max} = 0.99
22118 measured reflections
4957 independent reflections
3436 reflections with $I > 2\sigma(I)$
R_{int} = 0.095

θ_{max} = 25.0°, θ_{min} = 3.9°
h = −9→9
k = −10→10
l = −23→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.145
S = 1.03
4957 reflections
352 parameters
2 restraints
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Absolute structure: Absolute structure assigned by comparison with related compounds of the same origin

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
O1	0.0248 (4)	1.0961 (3)	0.21889 (15)	0.0520 (8)
O2	0.2942 (4)	1.1168 (4)	0.30509 (17)	0.0647 (9)
H2	0.295 (6)	1.116 (7)	0.2617 (8)	0.078*
O1A	0.0848 (3)	0.8933 (4)	0.34684 (16)	0.0577 (8)
O2A	−0.0751 (5)	0.7790 (5)	0.4214 (2)	0.0928 (14)
O1B	−0.3168 (4)	1.1961 (4)	0.17183 (15)	0.0556 (8)
O2B	−0.5950 (4)	1.1608 (5)	0.15481 (19)	0.0902 (13)
O1C	−0.2916 (4)	1.4503 (4)	0.25353 (19)	0.0685 (10)
O2C	−0.2108 (6)	1.5734 (5)	0.1618 (2)	0.0903 (13)
C1	−0.1357 (5)	1.3667 (6)	0.2572 (3)	0.0554 (12)
H1A	−0.100464	1.351650	0.210076	0.067*
C2	0.0049 (7)	1.4439 (6)	0.2974 (3)	0.0705 (15)
H2A	−0.024269	1.456356	0.344936	0.085*
H2B	0.022696	1.539141	0.277618	0.085*
C3	0.1668 (7)	1.3525 (7)	0.2944 (3)	0.0761 (16)
H3C	0.197293	1.345427	0.246721	0.091*
H3D	0.258281	1.402147	0.320050	0.091*
C4	0.1497 (5)	1.1996 (6)	0.3236 (2)	0.0547 (12)
C5	−0.0144 (5)	1.1228 (5)	0.2903 (2)	0.0478 (11)
C6	−0.0618 (5)	0.9740 (5)	0.3191 (2)	0.0506 (12)
H6	−0.145201	0.985082	0.354345	0.061*
C7	−0.1427 (5)	0.9053 (5)	0.2550 (3)	0.0535 (11)
H7	−0.152155	0.799690	0.260079	0.064*
C8	−0.3177 (6)	0.9766 (6)	0.2449 (3)	0.0584 (13)

H8A	−0.386279	0.944656	0.282048	0.070*
H8B	−0.371181	0.940789	0.202050	0.070*
C9	−0.3213 (6)	1.1432 (5)	0.2429 (2)	0.0534 (12)
H9	−0.429346	1.174352	0.260621	0.064*
C10	−0.1777 (5)	1.2181 (5)	0.2877 (2)	0.0438 (10)
C11	−0.0211 (6)	0.9451 (5)	0.1992 (2)	0.0554 (12)
C12	0.1405 (6)	0.8529 (7)	0.2016 (3)	0.0705 (15)
H12A	0.220192	0.894588	0.171576	0.106*
H12B	0.113243	0.755817	0.186626	0.106*
H12C	0.189366	0.850391	0.247954	0.106*
C13	−0.0937 (7)	0.9451 (7)	0.1252 (3)	0.0756 (16)
H13A	−0.188213	1.010548	0.121042	0.113*
H13B	−0.130598	0.848786	0.112766	0.113*
H13C	−0.008165	0.975860	0.095086	0.113*
C14	0.1606 (6)	1.2019 (7)	0.4023 (2)	0.0729 (15)
H14A	0.127127	1.109054	0.419467	0.109*
H14B	0.086573	1.275794	0.418387	0.109*
H14C	0.274948	1.222471	0.418517	0.109*
C15	−0.2541 (6)	1.2399 (6)	0.3599 (2)	0.0658 (14)
H15A	−0.165309	1.265718	0.393399	0.099*
H15B	−0.306657	1.151293	0.373703	0.099*
H15C	−0.337074	1.316124	0.356861	0.099*
C1A	0.0603 (6)	0.7976 (5)	0.3975 (2)	0.0529 (12)
C2A	0.2169 (6)	0.7201 (6)	0.4179 (2)	0.0522 (11)
C3A	0.3725 (6)	0.7588 (6)	0.3934 (3)	0.0695 (15)
H3A	0.380130	0.837189	0.363455	0.083*
C4A	0.5171 (7)	0.6803 (8)	0.4137 (3)	0.0844 (17)
H4A	0.621311	0.705412	0.397100	0.101*
C5A	0.5055 (9)	0.5668 (8)	0.4580 (4)	0.092 (2)
H5A	0.602884	0.515738	0.471944	0.110*
C6A	0.3527 (9)	0.5259 (7)	0.4825 (3)	0.0842 (18)
H6A	0.346144	0.447350	0.512347	0.101*
C7A	0.2103 (7)	0.6026 (6)	0.4622 (2)	0.0644 (13)
H7A	0.106588	0.575161	0.478625	0.077*
C1B	−0.4618 (6)	1.2036 (6)	0.1345 (3)	0.0594 (12)
C2B	−0.4429 (7)	1.2696 (7)	0.0667 (3)	0.0689 (15)
C3B	−0.5647 (10)	1.2909 (11)	0.0169 (4)	0.129 (3)
H3B	−0.676901	1.263268	0.021008	0.155*
C4B	−0.5098 (10)	1.3543 (11)	−0.0378 (3)	0.116 (3)
H4B	−0.572834	1.379679	−0.077893	0.139*
O3B	−0.3399 (11)	1.3757 (11)	−0.0238 (4)	0.189 (3)
C5B	−0.2985 (9)	1.3237 (10)	0.0408 (3)	0.107 (3)
H5B	−0.191436	1.324767	0.063075	0.129*
C1C	−0.3168 (9)	1.5449 (6)	0.2006 (4)	0.0775 (17)
C2C	−0.4930 (8)	1.6027 (7)	0.1984 (4)	0.101 (2)
H2CA	−0.498547	1.690865	0.171930	0.152*
H2CB	−0.525040	1.622173	0.244531	0.152*
H2CC	−0.568925	1.532252	0.177284	0.152*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0489 (17)	0.057 (2)	0.0503 (17)	−0.0066 (16)	0.0075 (12)	−0.0016 (15)
O2	0.0402 (18)	0.083 (3)	0.070 (2)	−0.0003 (17)	0.0032 (16)	0.007 (2)
O1A	0.0417 (17)	0.063 (2)	0.068 (2)	0.0055 (15)	0.0036 (14)	0.0203 (17)
O2A	0.059 (2)	0.112 (3)	0.110 (3)	0.015 (2)	0.026 (2)	0.059 (3)
O1B	0.0469 (18)	0.063 (2)	0.0570 (18)	0.0009 (16)	0.0014 (14)	0.0052 (16)
O2B	0.053 (2)	0.134 (4)	0.082 (2)	−0.010 (2)	−0.0073 (18)	0.019 (2)
O1C	0.070 (2)	0.057 (2)	0.079 (2)	0.0140 (19)	0.0037 (17)	0.010 (2)
O2C	0.099 (3)	0.076 (3)	0.095 (3)	−0.004 (3)	0.002 (2)	0.025 (2)
C1	0.048 (3)	0.056 (3)	0.061 (3)	0.003 (2)	0.001 (2)	0.003 (2)
C2	0.074 (4)	0.056 (3)	0.080 (4)	−0.005 (3)	−0.009 (3)	−0.005 (3)
C3	0.075 (4)	0.075 (4)	0.077 (4)	−0.026 (3)	−0.011 (3)	0.005 (3)
C4	0.045 (3)	0.060 (3)	0.059 (3)	−0.008 (2)	−0.0020 (19)	0.002 (3)
C5	0.043 (2)	0.054 (3)	0.047 (3)	−0.006 (2)	0.0058 (18)	0.000 (2)
C6	0.037 (2)	0.051 (3)	0.064 (3)	0.002 (2)	0.005 (2)	0.012 (2)
C7	0.042 (2)	0.042 (3)	0.076 (3)	−0.006 (2)	−0.003 (2)	0.001 (2)
C8	0.048 (3)	0.058 (3)	0.069 (3)	−0.009 (2)	−0.002 (2)	0.008 (3)
C9	0.048 (3)	0.060 (3)	0.053 (3)	−0.010 (2)	0.0042 (19)	0.016 (2)
C10	0.045 (2)	0.043 (2)	0.044 (2)	−0.001 (2)	0.0054 (17)	0.001 (2)
C11	0.051 (3)	0.048 (3)	0.066 (3)	0.003 (2)	−0.002 (2)	−0.005 (2)
C12	0.068 (3)	0.075 (4)	0.069 (3)	0.018 (3)	0.010 (3)	0.003 (3)
C13	0.081 (4)	0.077 (4)	0.068 (3)	0.009 (3)	−0.006 (3)	−0.015 (3)
C14	0.066 (3)	0.088 (4)	0.063 (3)	0.000 (3)	−0.011 (2)	0.000 (3)
C15	0.066 (3)	0.071 (4)	0.061 (3)	0.015 (3)	0.007 (2)	0.005 (3)
C1A	0.047 (3)	0.055 (3)	0.057 (3)	−0.004 (2)	0.004 (2)	0.009 (2)
C2A	0.052 (3)	0.058 (3)	0.045 (2)	0.002 (2)	−0.0032 (19)	−0.006 (2)
C3A	0.048 (3)	0.077 (4)	0.083 (4)	0.004 (3)	−0.006 (2)	0.004 (3)
C4A	0.056 (3)	0.096 (5)	0.099 (4)	0.007 (3)	−0.009 (3)	0.001 (4)
C5A	0.085 (5)	0.096 (5)	0.091 (5)	0.035 (4)	−0.036 (4)	−0.019 (4)
C6A	0.106 (5)	0.068 (4)	0.076 (4)	0.029 (4)	−0.025 (4)	−0.006 (3)
C7A	0.078 (3)	0.065 (3)	0.050 (3)	0.005 (3)	0.001 (2)	−0.004 (3)
C1B	0.044 (3)	0.062 (3)	0.072 (3)	0.005 (3)	−0.001 (2)	0.005 (3)
C2B	0.068 (4)	0.082 (4)	0.055 (3)	0.007 (3)	−0.009 (3)	−0.001 (3)
C3B	0.099 (6)	0.177 (9)	0.108 (6)	−0.004 (5)	−0.028 (5)	0.043 (6)
C4B	0.097 (5)	0.190 (8)	0.056 (4)	−0.011 (5)	−0.030 (3)	0.042 (5)
O3B	0.258 (9)	0.213 (8)	0.098 (4)	−0.015 (8)	0.024 (5)	0.039 (5)
C5B	0.101 (5)	0.155 (8)	0.066 (4)	−0.015 (5)	0.007 (3)	0.020 (4)
C1C	0.093 (5)	0.054 (3)	0.084 (4)	0.002 (3)	−0.013 (4)	0.000 (3)
C2C	0.094 (5)	0.069 (4)	0.138 (6)	0.019 (4)	−0.019 (4)	0.010 (4)

Geometric parameters (Å, º)

O1—C5	1.457 (5)	C11—C12	1.533 (6)
O1—C11	1.480 (6)	C12—H12A	0.9600
O2—C4	1.435 (6)	C12—H12B	0.9600
O2—H2	0.842 (14)	C12—H12C	0.9600

O1A—C1A	1.341 (5)	C13—H13A	0.9600
O1A—C6	1.454 (5)	C13—H13B	0.9600
O2A—C1A	1.202 (5)	C13—H13C	0.9600
O1B—C1B	1.325 (5)	C14—H14A	0.9600
O1B—C9	1.464 (5)	C14—H14B	0.9600
O2B—C1B	1.209 (6)	C14—H14C	0.9600
O1C—C1C	1.353 (7)	C15—H15A	0.9600
O1C—C1	1.451 (6)	C15—H15B	0.9600
O2C—C1C	1.186 (7)	C15—H15C	0.9600
C1—C2	1.500 (7)	C1A—C2A	1.465 (6)
C1—C10	1.534 (7)	C2A—C7A	1.384 (7)
C1—H1A	0.9800	C2A—C3A	1.389 (7)
C2—C3	1.535 (8)	C3A—C4A	1.391 (7)
C2—H2A	0.9700	C3A—H3A	0.9300
C2—H2B	0.9700	C4A—C5A	1.358 (9)
C3—C4	1.526 (8)	C4A—H4A	0.9300
C3—H3C	0.9700	C5A—C6A	1.374 (10)
C3—H3D	0.9700	C5A—H5A	0.9300
C4—C14	1.525 (7)	C6A—C7A	1.368 (7)
C4—C5	1.583 (6)	C6A—H6A	0.9300
C5—C6	1.532 (6)	C7A—H7A	0.9300
C5—C10	1.559 (6)	C1B—C2B	1.464 (7)
C6—C7	1.507 (7)	C2B—C3B	1.340 (8)
C6—H6	0.9800	C2B—C5B	1.365 (8)
C7—C11	1.529 (7)	C3B—C4B	1.306 (10)
C7—C8	1.535 (6)	C3B—H3B	0.9300
C7—H7	0.9800	C4B—O3B	1.370 (9)
C8—C9	1.534 (7)	C4B—H4B	0.9300
C8—H8A	0.9700	O3B—C5B	1.364 (9)
C8—H8B	0.9700	C5B—H5B	0.9300
C9—C10	1.554 (6)	C1C—C2C	1.489 (9)
C9—H9	0.9800	C2C—H2CA	0.9600
C10—C15	1.567 (6)	C2C—H2CB	0.9600
C11—C13	1.517 (7)	C2C—H2CC	0.9600

C5—O1—C11	110.0 (3)	C11—C12—H12A	109.5
C4—O2—H2	108 (4)	C11—C12—H12B	109.5
C1A—O1A—C6	117.6 (3)	H12A—C12—H12B	109.5
C1B—O1B—C9	117.9 (3)	C11—C12—H12C	109.5
C1C—O1C—C1	118.0 (4)	H12A—C12—H12C	109.5
O1C—C1—C2	112.2 (4)	H12B—C12—H12C	109.5
O1C—C1—C10	106.9 (3)	C11—C13—H13A	109.5
C2—C1—C10	113.1 (4)	C11—C13—H13B	109.5
O1C—C1—H1A	108.2	H13A—C13—H13B	109.5
C2—C1—H1A	108.2	C11—C13—H13C	109.5
C10—C1—H1A	108.2	H13A—C13—H13C	109.5
C1—C2—C3	108.5 (4)	H13B—C13—H13C	109.5
C1—C2—H2A	110.0	C4—C14—H14A	109.5

C3—C2—H2A	110.0	C4—C14—H14B	109.5
C1—C2—H2B	110.0	H14A—C14—H14B	109.5
C3—C2—H2B	110.0	C4—C14—H14C	109.5
H2A—C2—H2B	108.4	H14A—C14—H14C	109.5
C4—C3—C2	113.6 (4)	H14B—C14—H14C	109.5
C4—C3—H3C	108.8	C10—C15—H15A	109.5
C2—C3—H3C	108.8	C10—C15—H15B	109.5
C4—C3—H3D	108.8	H15A—C15—H15B	109.5
C2—C3—H3D	108.8	C10—C15—H15C	109.5
H3C—C3—H3D	107.7	H15A—C15—H15C	109.5
O2—C4—C3	108.1 (4)	H15B—C15—H15C	109.5
O2—C4—C14	104.7 (4)	O2A—C1A—O1A	122.9 (4)
C3—C4—C14	110.9 (5)	O2A—C1A—C2A	125.7 (4)
O2—C4—C5	107.9 (4)	O1A—C1A—C2A	111.4 (4)
C3—C4—C5	110.4 (4)	C7A—C2A—C3A	118.5 (5)
C14—C4—C5	114.5 (4)	C7A—C2A—C1A	119.3 (4)
O1—C5—C6	105.3 (3)	C3A—C2A—C1A	122.3 (4)
O1—C5—C10	106.4 (3)	C2A—C3A—C4A	119.9 (5)
C6—C5—C10	107.3 (3)	C2A—C3A—H3A	120.0
O1—C5—C4	104.5 (3)	C4A—C3A—H3A	120.0
C6—C5—C4	117.5 (4)	C5A—C4A—C3A	119.8 (6)
C10—C5—C4	114.9 (4)	C5A—C4A—H4A	120.1
O1A—C6—C7	112.6 (4)	C3A—C4A—H4A	120.1
O1A—C6—C5	112.7 (3)	C4A—C5A—C6A	121.3 (6)
C7—C6—C5	100.1 (4)	C4A—C5A—H5A	119.3
O1A—C6—H6	110.3	C6A—C5A—H5A	119.3
C7—C6—H6	110.3	C5A—C6A—C7A	119.0 (6)
C5—C6—H6	110.3	C5A—C6A—H6A	120.5
C6—C7—C11	103.2 (3)	C7A—C6A—H6A	120.5
C6—C7—C8	105.4 (4)	C6A—C7A—C2A	121.6 (5)
C11—C7—C8	113.8 (4)	C6A—C7A—H7A	119.2
C6—C7—H7	111.3	C2A—C7A—H7A	119.2
C11—C7—H7	111.3	O2B—C1B—O1B	123.2 (5)
C8—C7—H7	111.3	O2B—C1B—C2B	124.1 (4)
C7—C8—C9	116.5 (4)	O1B—C1B—C2B	112.7 (4)
C7—C8—H8A	108.2	C3B—C2B—C5B	105.3 (6)
C9—C8—H8A	108.2	C3B—C2B—C1B	127.1 (6)
C7—C8—H8B	108.2	C5B—C2B—C1B	127.6 (5)
C9—C8—H8B	108.2	C4B—C3B—C2B	113.2 (7)
H8A—C8—H8B	107.3	C4B—C3B—H3B	123.4
O1B—C9—C8	110.8 (4)	C2B—C3B—H3B	123.4
O1B—C9—C10	109.0 (3)	C3B—C4B—O3B	105.5 (6)
C8—C9—C10	114.7 (4)	C3B—C4B—H4B	127.2
O1B—C9—H9	107.4	O3B—C4B—H4B	127.2
C8—C9—H9	107.4	C5B—O3B—C4B	108.4 (6)
C10—C9—H9	107.4	O3B—C5B—C2B	107.6 (6)
C1—C10—C9	110.3 (3)	O3B—C5B—H5B	126.2
C1—C10—C5	108.6 (3)	C2B—C5B—H5B	126.2

C9—C10—C5	110.3 (4)	O2C—C1C—O1C	122.9 (6)
C1—C10—C15	109.4 (4)	O2C—C1C—C2C	126.5 (6)
C9—C10—C15	104.6 (3)	O1C—C1C—C2C	110.6 (6)
C5—C10—C15	113.6 (3)	C1C—C2C—H2CA	109.5
O1—C11—C13	108.6 (4)	C1C—C2C—H2CB	109.5
O1—C11—C7	101.4 (4)	H2CA—C2C—H2CB	109.5
C13—C11—C7	116.6 (4)	C1C—C2C—H2CC	109.5
O1—C11—C12	108.7 (4)	H2CA—C2C—H2CC	109.5
C13—C11—C12	107.5 (4)	H2CB—C2C—H2CC	109.5
C7—C11—C12	113.6 (4)		